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Review

# Lime mud from papermaking process as a potential ameliorant for pollutants at ambient conditions: a review

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ABSTRACT

Lime mud from papermaking process (LMP) is a solid waste originated from the causticization process. Due to fine particle size and high alkalinity of LMP, its recovery is expensive and adverse effect is still uncertain. This review presents several current techniques proposed for LMP utilization in order to minimize its toxic effect on the environment. Conventional uses such as soil amendments, landfill and building materials are continually conducted. Recently, novel utilization of LMP to immobilize and remove pollutants in different phases (liquid, solid and gas) has provided new opportunities for efficient removal of dye, organics, heavy metals, carbon dioxide and sulfur dioxide. Moreover, as an additive summarized in this review, LMP can enhance the performance of biological process for treating organic waste, and its available value would be potentially improved further.



## 1. Introduction

Pulp and paper mills have produced large amounts of pulp annually (He et al., 2009; Nurmesniemi et al., 2007; Zhou et al., 2012). As the second largest producer of paper globally, for instance, China produces approximately 50 million tons of papers per year that accounts for over 50 wt% in terms of the global yield (He and Barr, 2004). However, masses of inorganic (e.g. ash, dregs and grits) and organic residues could be generated in bleached kraft pulp, causing serious environmental and ecological problems. It is estimated that about 0.47 $m^3$ of lime mud from papermaking process (LMP) can be produced from one ton of pulp (Wirojanagud et al., 2004). In addition, the production of LMP in China in 2011 reached near to 10 million tons and it is increasing with expanded need for paper (Sun et al., 2013).

Production and characteristics of LMP are described in Table 1. Due to high alkalinity and mineralogical properties, LMP is classified as toxic industrial waste, which needs to be treated before discharge. Large amounts and high alkalinity of LMP make it a challenging globally environmental issue (Ren, 1998). Although landfill is an ordinary method available to manage solid waste (He et al., 2009), it results in land occupation, waste of available resource and environmental pollution (Huber et al., 2014). The issues are presented as follows, a) intake of fine particulate matter by human and animals; b) underlying risk posed by landfill leachates to rivers and groundwater; c) ecotoxicological effects on plants and adverse impact on soils; and d) production of fine dust in dry or windy conditions (Liu et al., 2011). Moreover, landfill is not considered as a suitable method to dispose of LMP (Monte et al., 2009; Nurmesniemi et al., 2007). Therefore, improvements in management, application and cost-effective resourcization of LMP are essential for the success of cleaner treatment (Ren, 1998).

Approaches to remediate LMP are depicted in Table 2. It was found that LMP can be used as building materials, but more desalting, dewatering, drying and sintering processes are highly needed when it is introduced to manufacture sintered products (e.g. bricks, cements and concretes) with higher costs and energy consumption. LMP, as an alkaline material, can be utilized in agricultural soils to control acid mine drainage (Bellaloui et al., 1999) and ameliorate acid soils. Furthermore, precipitation or immobilization of heavy metals using LMP has been also investigated, which indicated a high removal efficiency during wastewater treatment

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**Table 1**
LMP source and its high alkalinity, saline properties with composition of heavy metals.

| LMP source | | pH | Ca (wt%) | Toxic metals | References |
|---|---|---|---|---|---|
| USA | Alabama | 13 ± 0.46 | – | Cd, Cr, Cu, Ni, Pb, Zn | He et al. (2009) |
| China | Shandong | 11.5 | 35.44 | Cu, Mn | Zhang et al. (2013) |
| Thailand | Prachinburi | 12.1 | – | Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn | Sthiannopkao and Sreesai (2009) |
| Brazil | Curitiba | – | 36.02 | Mn | Martins et al. (2007) |
| Finland | Kemi | 12.8 | 40.1–43.9 | Cu, Zn | Pöykiö et al. (2006) |
| Spain | Huelva | 11.96 | 59.0 | As, Cd, Cu, Cr, Ni, Zn | Pérez-López et al. (2010) |

process (Sun et al., 2013). However, LMP recycle is limited by the presence of chlorides, and it would better store near industrial facilities. With environmental concerns growing, the exploitation of LMP is continually studied, while few feasible, eco-friendly and cost-effective approaches have been found.

This review summarizes the chemical characteristics and environmental impact of LMP. As a low-cost absorbent or agent, the current progresses on LMP potential applications such as wastewater and air pollution, remediation of contaminated soils, and biotreatment of organic waste are also reviewed in details.

## 2. Production and characteristics of LMP

### 2.1. LMP production

Pulp and paper plants are primary sources of LMP in the causticization process versus mechanical, chemi-mechanical and chemical methods, respectively. Kraft process, the most dominating chemical pulp, is used to dispose of wood species in spite of pollution problems posed by malodorous compounds. The flow sheet of LMP production in kraft pulp papermaking process has been shown by Martins et al. (2007), together with Eq. (1) (Cheng et al., 2009), as seen from Table 3.

In general, precipitated calcium carbonate (PCC) is generally produced from mined, crushed calcium carbonate ($CaCO_3$) and calcium silicates, with a higher purity of $CaCO_3$ than that of ground $CaCO_3$ (GCC) from a controlled synthesis through calcination and hydratization, filtration and carbonation. There are several various types of PCC grades, but the purity of PCC is usually over 99 wt% with density of 2700 kg/m$^3$ (Teir et al., 2005). In papermaking process, PCC could enhance paper bulk, brightness, light scattering and printability as a filler agent. However, the calcination of $CaCO_3$ requires about the external heat of 2669 kJ/kg $CaCO_3$ (with an initial temperature of 25 °C) at 900 °C (Teir et al., 2005), Consequently, it causes a high cost and energy consumption.

### 2.2. Characteristics of LMP

Chemical and mineralogical analysis reveals that LMP is primarily composed of $CaCO_3$, along with unslaked CaO and $Ca(OH)_2$, and trace mineral elements, e.g. Mg, K, Na, Cr, Mn, and Fe (He et al., 2009; Martins et al., 2007; Pérez-López et al., 2010; Pöykiö et al., 2006; Sthiannopkao and Sreesai, 2009; Zhang et al., 2013). It has a pH range of 9.7–13.5 (Catalan and Kumari, 2005; He et al., 2009). An elemental characteristics of LMP displayed that the major chemical component of LMP is calcium (Ca) in the range of 10–38 wt%, and the formula of $Ca_{(1-x)}Mg_xCO_3$ could be represented for LMP with Mg in calcite structures (Martins et al., 2007). LMP composition originated from pulp and papermaking mills varies in different feedstock and processes. Furthermore, LMP can be activated by acidification with concentrated sulfuric acid or diluted hydrochloric acid. Most of dissolved metal oxides convert to cation forms except for silicon dioxide that can be recovered. Multiple cavities are newly formed with the dissolution of metal oxides, which facilitates adsorption and precipitation to organics synergetically in wastewater.

The particle size distribution of LMP ranged from 1 to 100 μm with a median size of 15 μm (Pérez-López et al., 2008). The specific surface area of LMP is 2.3–4.7 m$^2$/g, with the density range of 2620–2660 kg/m$^3$ and less than 5% of porosity (Eriksson et al., 1996).

### 2.3. LMP and limestone

Although LMP and limestone both contain lots of $CaCO_3$, they are different in microstructure and the content of alkali metal ions (Li et al., 2012). LMP contains slight amounts of compounds (e.g. $Na_2O$, $K_2O$, $Fe_2O_3$, and $SiO_2$) that are still higher than that of natural limestone. They may play an important role in the sulfation behavior with LMP. Previous studies have shown that the addition of alkali metal ions could improve the sulfur capture capacity of limestone (Laursen et al., 2001, 2003), and the presence of $Fe_2O_3$ had a positive effect on the performance of Ca-based adsorbents during $SO_2$ capture (Siagi et al., 2007).

## 3. Wastewater treatment using LMP

Attentions on evolving novel strategies and expanding applications for better disposal of LMP are increasingly paid. Environment-friendly, benign, and efficient applications of LMP such as ameliorants for contaminated soils and pollutants removal

**Table 2**
Different strategies of LMP applications.

| Strategies for treatment | Examples | References |
|---|---|---|
| Neutralization | Acidic wastewaters, oxidized mine tailings, acid soil, acid mine drainage | Bellaloui et al. (1999), Catalan and Kumari (2005), Monte et al. (2009), Nurmesniemi et al. (2007), Wirojanagud et al. (2004) |
| Addition to anaerobic digestion of biowaste | LMP as buffering and nutrient effects during anaerobic process | Zhang et al. (2013) |
| $CaCO_3$ recovery | Precipitated calcium carbonate (PCC) used as a filler | Martins et al. (2007) |
| Building materials | Bricks, cement, concrete | Monte et al. (2009) |
| Soil amendment | Alkaline fertilizer, contaminated soils by heavy metals | Hartley et al. (2004), Morris et al. (2000), Muse and Mitchell (1995), Wirojanagud et al. (2004) |
| Absorbents or precipitating agent | For wastewater, trace elements – heavy metals and metalloids | Hartley et al. (2004), Morris et al. (2000), Muse and Mitchell (1995), Wirojanagud et al. (2004) |
| Air pollution control | Carbon dioxide absorbent, de-sulfurization | Li et al. (2012), Sun et al. (2013) |

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